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ADSORPTION OF PHENOL, CRESOLS, AND BENZYL ALCOHOL FROM AQUEOUS SOLUTION BY SILICALITE

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Silicalite, an aluminium-free analogue of zeolite ZSM-5, selectively adsorbs phenol, cresols, and benzyl alcohol from aqueous solution and its adsorption capacity is superior to that of ZSM-5. The amount of these organic molecules adsorbed is benzyl alcohol ≃ *p*- > *m*- > *o*-cresol >> phenol in the order.

Silicalite, first developed by Union Carbide Corp., is an aluminium-free analogue of zeolite ZSM series.[1,2] Thus far there are two kinds of that, *i.e.*, silicalite-1 and silicalite-2, which are structually corresponded to ZSM-5 (orthorhombic) and ZSM-11 (tetragonal), respectively.[3] The structure is a series of intersecting channels, straight and zigzag in silicalite-1[2] and straight only in silicalite-2.[3,4] Both channels are defined by 10-oxygen rings and capable of absorbing organic molecules up to ≃0.6 nm kinetic diameter.[2] More remarkable is that silicalite has a hydrophobic surface and high resistances for heat and acid because of the absence of aluminium ion in the frame-work.[2,5] Accordingly, silicalite has the possibility of utilization as adsorbents for small organic molecules in water. On this subject two studies have been carried out. Milestone and Bibby[6] have investigated the adsorption properties of aliphatic alcohols (C_1–C_5-OH) from aqueous solution to develop an alternative process to distillation for concentration of alcohols from the dilute solutions such as fermentation liquors. Maddox[7] has shown that the adsorption of 1-butanol onto silicalite from practical fermentation liquors would be useful. A hydrophobic surface of silicalite can be used not only for concentration of aliphatic alcohols but also for adsorption of aromatic alcohols and their related compounds. The purpose of the present work is to investigate the use of silicalite to adsorb phenol, cresols and benzyl alcohol from aqueous solution.

The reaction materials used for preparation of silicalite were colloidal silica (Snowtex-30 from Nissan Chemical Ind., Ltd.; 30% SiO_2), sodium hydroxide, and *tetra*-propylammonium hydroxide (10% TPAOH) (both Wako Pure Chemical Ind., Ltd., guaranteed reagents).

Silicalite was synthesized fundamentally according to the patent of Union Carbide Corp.[1] However, the synthesis conditions were varied to obtain silicalite which has the highest possible crystallinity and hydrophobic surface as follows:

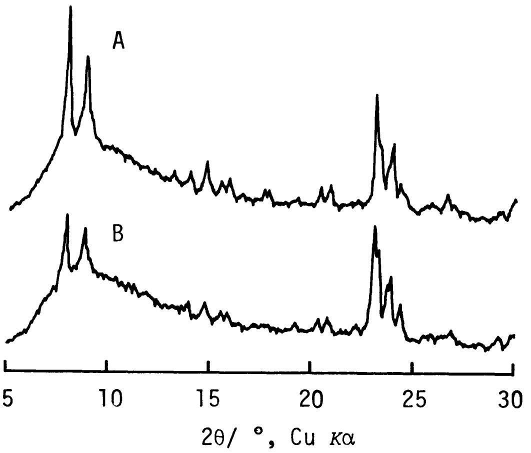

Fig. 1. X-Ray diffraction patterns of silicalite (A) and ZSM-5 (B).

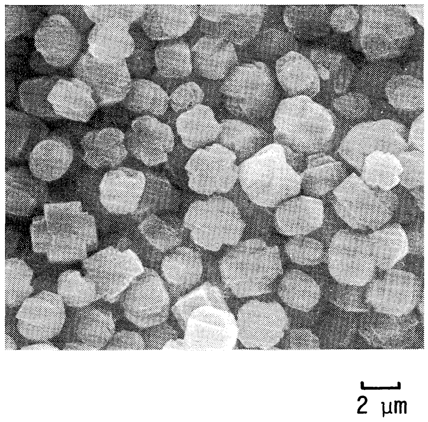

Fig. 2. Scanning electron micrograph of silicalite.

$(TPA)_2O/SiO_2$: 0.02–0.08, Na_2O/SiO_2: 0.065–0.26, H_2O/SiO_2: 10–40, temperature: 150–210 °C, time: 0.5–5 d.

Consequently, the following conditions were found to be most appropriate for this

[Composition $0.06(TPA)_2O$-$0.13Na_2O$-SiO_2-$20H_2O$; temperature 170 °C; time 3 d]

purpose. X-Ray diffraction pattern (Fig. 1-A) revealed that the resulting precursor has silicalite-1 structure. As can be seen in Fig. 2, the particle was twin up to 3 µm. Before being used in the adsorption experiment, the precursor was heated at 600 °C for 1 h to remove the obstructing organic compounds from its channel. The B.E.T. surface area of silicalite measured by N_2 adsorption at liquid nitrogen temperature was 297 $m^2\ g^{-1}$. ZSM-5 used for reference was prepared by the same method and had the similar crystal structure to that of silicalite as shown in Fig. 1-B (Surface area 273 $m^2\ g^{-1}$; SiO_2/Al_2O_3 ratio 38).

For the investigation of the determination of the adsorption isotherms, 0.1 g of adsorbent and 25 cm^3 of an organic compound solution of known initial concentration (C_0: mg dm^{-3}) were mechanically shaken in 50 cm^3 Erlenmeyer flasks at 25–45 °C for 20 h. 0.2 mol dm^{-3} HCl or NaOH was used for adjusting pH. The amount of organic molecule adsorbed (X: mg dm^{-3}) was calculated from the equilibrium concentration (C: mg dm^{-3}) of the centrifugate, which was determined by spectrophotometry at 240 nm (phenol and cresols) and 265 nm (benzyl alcohol).

It is generally known that, regardless of pH, benzyl alcohol exists in nonion form in an aqueous solution, whereas phenol and cresols dissociate into ions by alterations in pH. In order to clarify the effect of the existence form of the adsorbates, the effect of pH on the adsorbability was first investigated at 25 °C and the result is shown

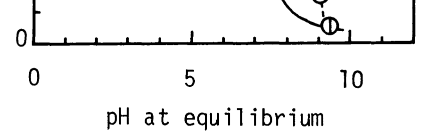

Fig. 3. Effect of pH on the adsorption of phenol (○), *m*-cresol (⦶), and benzyl alcohol (◑) on silicalite at 25 °C. C_0 (mg dm^{-3}) –○: 100, ⦶: 500, ◑: 1000.

in Fig. 3. The adsorbability of benzyl alcohol was independent of pH, whereas those of phenol and *m*-cresol (it has the lowest dissociation constant in cresol isomers) suddenly fell at above 8 and 7, respectively. This means that phenol and cresols can be adsorbed onto silicalite only in nonion form by the hydrophobic attractive force. In the following experiments, the pH of the solution was kept at lower than 7.

Figures 4 and 5 show the adsorption isotherms of phenol and benzyl alcohol on silicalite, respectively, together with those on ZSM-5. In all cases, the Freundlich isotherm[8)] may be applied in the form:

$$\log (X/M) = 1/n(\log C) + \log k$$

where n and k are constants and M is the amount of adsorbent added (g dm^{-3}). Table 1 gives the values of k and n, which were calculated from the intercept and slope of the isotherms in Figs. 4 and 5. Benzyl alcohol was adequately adsorbed on silicalite and its adsorbability was considerably higher than those of aliphatic alcohols reported by earlier workers.[6,7)] It can also be said that the adsorbability of phenol was apparently lower than that of benzyl alcohol. However, the n value of phenol was 2.40, which indicates that silicalite can also be used as an adsorbent for phenol. On the other hand, the adsorption capacity of ZSM-5 was lower than that of silicalite. In general, ZSM-5 has an electric charge because of the content of aluminium ion in its framework. Therefore, the competitive adsorption of water is facilitated in an aqueous solution according to the amount of the electric charge. It was thought to responsible for low adsorbability of organic molecule on ZSM-5. Figure 6 shows the adsorption isotherms of *p*-, *m*-, *o*-cresols on silicalite at 25 °C. They were adsorbed on silicalite very much. The values of k and n are also given in Table 1. The adsorbabilities of cresols were considerably higher than that of phenol, but similar to

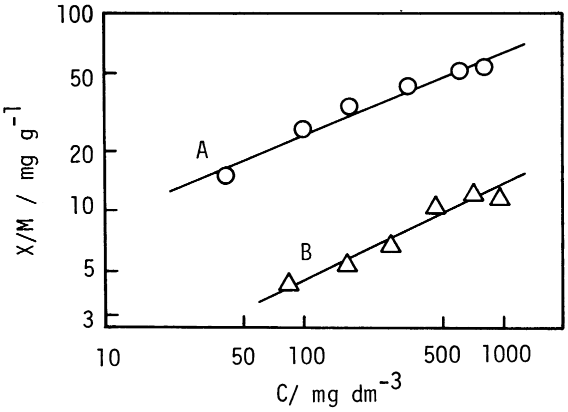

Fig. 4. Adsorption isotherms of phenol on silicalite (A) and ZSM-5 (B) at 25 °C.

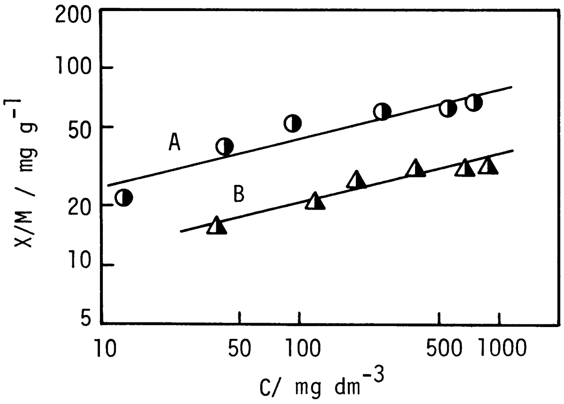

Fig. 5. Adsorption isotherms of benzyl alcohol on silicalite (A) and ZSM-5 (B) at 25 °C.

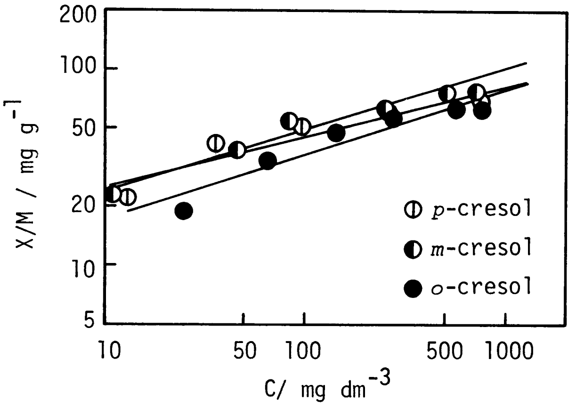

Fig. 6. Adsorption isotherms of cresols on silicalite at 25 °C.

Table 1. Adsorption data of phenol, cresols, and benzyl alcohol on silicalite and zeolite ZSM-5

Adsorbent	Adsorbate	Additive	Temperature °C	k mg g^{-1}	n	Adsorbate molecule per unit cell$^{a)}$
silicalite	phenol	0	25	3.53	2.40	2.88
	〃	0	35	3.14	2.33	2.77
	〃	0	45	1.48	1.86	2.56
	〃	0.4 M$^{b)}$ NaCl	25	3.22	2.32	2.87
	〃	0.4 M Na_2SO_4	25	4.46	2.58	3.04
	benzyl alcohol	0	25	14.0	3.98	3.56
	p-cresol	0	25	14.3	3.97	3.65
	m-cresol	0	25	12.5	3.42	4.10
	o-cresol	0	25	7.91	2.99	3.37
ZSM-5	phenol	0	25	0.53	2.17	0.58
	benzyl alcohol	0	25	6.84	4.17	1.65

a) The unit cell composition for silicalite and ZSM-5 can be expressed as $[Na_nAl_nSi_{96-n}O_{192}]$.[2)] The data were calculated from the adsorbed amount at C=500 mg dm^{-3}. b) M = mol dm^{-3}.

that of benzyl alcohol. This result indicates that the increase of a $-CH_2-$ group gives equivalent increase in the adsorbability. However, the position of $-CH_2-$ group makes some difference in the adsorbability, which being as *p*- > *m*- > *o*-cresol in the order. This difference was thought to be caused by the size effect and was in agreement with the adsorption properties of cresols in organic solvent on ZSM-5.[9)]

The effects of temperature (35 and 45 °C) and addition of inorganic salts (0.4 mol dm^{-3} NaCl and Na_2SO_4) on the adsorbability of phenol are also given in Table 1. The adsorbability decreased with increasing temperature and slightly increased by the coexistence of inorganic salts. Same tendency was also observed on the adsorption of cresols and benzyl alcohol. The number of adsorbate molecule per unit cell was also given in Table 1.

On the basis of the results, it was concluded that silicalite selectively adsorbs small organic molecules from the aqueous solutions. The fact that silicalite is pure SiO_2 would give it a long life as adsorbent and an easy reactivation by heating. Studies concerning that are currently under way.

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